Unclassified

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# REPORT DOCUMENTATION PAGE

**AD-A197 872** CTE

AUG 1 9 1988

| | |
|---|---|
| 1b. RESTRICTIVE MARKINGS | |
| 2b. DECLASSIFICATION / DOWNGRADING SCHEDULE | 3. DISTRIBUTION / AVAILABILITY OF REPORT |

| 4. PERFORMING ORGANIZATION REPORT NUMBER(S) | 5. MONITORING ORGANIZATION REPORT NUMBER(S) |
|---|---|
| AFGL-TR-88-0173 | |

| 6a. NAME OF PERFORMING ORGANIZATION | 6b. OFFICE SYMBOL (If applicable) | 7a. NAME OF MONITORING ORGANIZATION |
|---|---|---|
| Air Force Geophysics Laboratory | LID | |

| 6c. ADDRESS (City, State, and ZIP Code) | 7b. ADDRESS (City, State, and ZIP Code) |
|---|---|
| Hanscom AFB Massachusetts, 01730-5000 | |

| 8a. NAME OF FUNDING / SPONSORING ORGANIZATION | 8b. OFFICE SYMBOL (If applicable) | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER |
|---|---|---|
| | | |

| 8c. ADDRESS (City, State, and ZIP Code) | 10 SOURCE OF FUNDING NUMBERS | | | |
|---|---|---|---|---|
| | PROGRAM ELEMENT NO | PROJECT NO. | TASK NO. | WORK UNIT ACCESSION NO |
| | 61102F | 2303 | G1 | 12 |

11. TITLE (Include Security Classification)
Chemical Pathways for Deuterium Fractionation in Interstellar Molecules

12. PERSONAL AUTHOR(S)
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| 13a. TYPE OF REPORT | 13b. TIME COVERED | | 14. DATE OF REPORT (Year, Month, Day) | 15. PAGE COUNT |
|---|---|---|---|---|
| Reprint | FROM _____ | TO _____ | 1988 August 15 | 7 |

16 SUPPLEMENTARY NOTATION *Chemistry Dept, Brandeis University, Waltham, MA 02254, **Department of Space Research, University of Birmingham, Birmingham B152TT UK #Institute for Experimental Physics University of Innstruck Karl Schoneherrstrasse 3 A6020 Innsbruck Austria (See reverse)

| 17 | COSATI CODES | | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) |
|---|---|---|---|
| FIELD | GROUP | SUB-GROUP | Ion-Molecule Reactions, Hydrogen Atom Exchange, Proton Transfer, Isotope Exchange, Astrochemistry, Reaction's |

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

ABSTRACT. The formation of deuterated interstellar molecules is considered. This contribution (which, in the summarizing remarks of the conference, was admonished for being itself admonitory) has a simple purpose — to apply gas-phase ion chemistry to distinguish deuterium exchange reactions that can occur from those that cannot. Thus the exoergic reaction $HCO^+ + D \rightarrow DCO^+ + H$ is facile whereas the exoergic reaction $HCO^+ + HD \xrightarrow{x} DCO^+ + H_2$ is not. Forbidden pathways involve energy barriers that can result from both reactants showing filled valence electron shells. A procedure is outlined for identifying such.

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

| 20. DISTRIBUTION / AVAILABILITY OF ABSTRACT | 21. ABSTRACT SECURITY CLASSIFICATION |
|---|---|
| ☐ UNCLASSIFIED/UNLIMITED  ☒ SAME AS RPT  ☐ DTIC USERS | Unclassified |

| 22a. NAME OF RESPONSIBLE INDIVIDUAL | 22b. TELEPHONE (Include Area Code) | 22c. OFFICE SYMBOL |
|---|---|---|
| John F. Paulson | (617) 377-3124 | LID |

**DD FORM 1473, 84 MAR**   83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

Cont. of Block 16

Reprinted from Rate Coefficients in Astrochemistry, 201-207, T.J. Millar and
D.A. Williams (eds.)

# AFGL-TR-88-0173

## CHEMICAL PATHWAYS FOR DEUTERIUM FRACTIONATION IN INTERSTELLAR MOLECULES

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ABSTRACT. The formation of deuterated interstellar molecules is considered. This contribution (which, in the summarizing remarks of the conference, was admonished for being itself admonitory) has a simple purpose — to apply gas-phase ion chemistry to distinguish deuterium exchange reactions that *can* occur from those that *cannot*. Thus the exoergic reaction $HCO^+ + D \rightarrow DCO^+ + H$ is facile whereas the exoergic reaction $HCO^+ + HD \xrightarrow{x} DCO^+ + H_2$ is not. Forbidden pathways involve energy barriers that can result from both reactants showing filled valence electron shells. A procedure is outlined for identifying such.

## 1.    FRACTIONATION OF DEUTERIUM IN INTERSTELLAR MOLECULES

The fractionation of deuterium in interstellar molecules continues to excite considerable interest.[1-3] Cosmologists identify the cosmic D/H ratio as a parameter critical to the assessment of cosmological models. Astrophysicists can use the isotopic ratio of species found in interstellar clouds as a probe of the conditions in those clouds. Isotopic abundances can help ion chemists to map synthetic pathways for forming interstellar molecules. Finally to chemical kineticists, interested in the formation of interstellar molecules at temperatures approaching absolute zero, isotope effects offer a unique challenge — what is a minor perturbation at 300 K must exercise a profound influence at 10 K. Thus[4] the equilibrium constant for the reaction

$$HCO^+ + D = DCO^+ + H \qquad -\Delta H^\circ/R \cong 800 \text{ K} \qquad (1)$$

is ~ 6 at 300 K but at 10 K becomes ~$10^{33}$ !

Eleven deuterated species have been identified [5,6] in interstellar space:

Molecules:    HD, HDO, $NH_2D$, CCD, DCN, DNC, HDCO, $CH_3OD$, $C_3HD$, $DC_3N$, $DC_5N$
Ions:    $H_2D^+$, $N_2D^+$, $DCO^+$

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The deuterium fractionation observed for these species must be measured against the benchmark of the cosmic D/H ratio and this is illustrated[7] for three examples below:

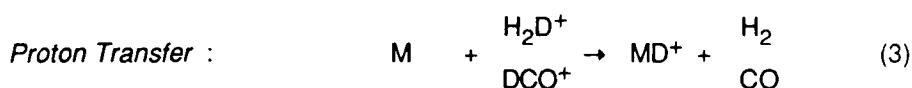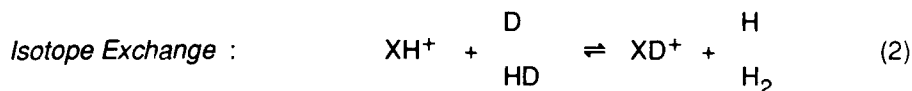| | | | |
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| Cosmic D/H ratio | | $\sim 2 \times 10^{-5}$ | |
| $DCO^+/HCO^+$ | $2 \times 10^{-4}$ | $\leftrightarrow$ | $1.4 \times 10^{-2}$ |
| DCN/HCN | $1.4 \times 10^{-3}$ | $\leftrightarrow$ | $1.2 \times 10^{-2}$ |
| DNC/HNC | 0.05 | $\leftrightarrow$ | 2.5 |

In general the extent of fractionation depends upon the location of the interstellar cloud. In many cases, the data confirm the thermodynamic expectation that the colder the cloud, the greater will be the fractionation. Yet in some notable cases, they do not.[8]

## 2. CHEMICAL PATHWAYS FOR DEUTERATING INTERSTELLAR MOLECULES

From the reaction sequence proposed for the synthesis of interstellar molecules in dense clouds,[3] it is straightforward to predict how deuterated species of increasing complexity could be formed. The starting material must be atomic deuterium, subsequently ionized by photoionization or charge exchange. This can react to form HD, which in turn can form $H_2D^+$ and $CH_2D^+$. The $H_2D^+$ can then form $DCO^+$ and so on. In this way a set of deuterated reactants is established — D, HD, $H_2D^+$, $DCO^+$, $CH_2D^+$ etc — that themselves can act as agents for deuterating interstellar molecules.

| Species | Formation | Reaction Type |
|---|---|---|
| D | *Big Bang* | |
| HD | $D^+ + H_2 = HD + H^+$ | Isotope Exchange |
| $H_2D^+$ | $H_3^+ + HD = H_2D^+ + H_2$ | Isotope Exchange |
| $DCO^+$ | $H_2D^+ + CO = DCO^+ + H_2$ | Proton Transfer |
| $CH_2D^+$ | $CH_3^+ + HD = CH_2D^+ + H_2$ | Isotope Exchange |

These species — D, HD, $H_2D^+$, $DCO^+$, $CH_2D^+$ etc — can incorporate deuterium by different chemical reactions, such as isotope exchange, proton transfer, association, dissociative recombination, etc. We can illustrate this by writing general equations for two of these reaction types below — isotope exchange and proton transfer — using two of the deuterating species for each reaction — D and HD for isotope exchange and $H_2D^+$ and $DCO^+$ for proton transfer.

$$\textit{Isotope Exchange}: \quad XH^+ + \begin{matrix} D \\ HD \end{matrix} \rightleftharpoons XD^+ + \begin{matrix} H \\ H_2 \end{matrix} \qquad (2)$$

$$\textit{Proton Transfer}: \quad M + \begin{matrix} H_2D^+ \\ DCO^+ \end{matrix} \rightarrow MD^+ + \begin{matrix} H_2 \\ CO \end{matrix} \qquad (3)$$

Here $XH^+$ is a cation containing at least one hydrogen site (which is exchanged for deuterium) while M is a neutral molecule (which incorporates deuterium by accepting a deuteron).

Isotope exchange would seem to be a particularly simple route for incorporating deuterium into interstellar molecules, for example by reaction (2) wherever D or HD are present.

## 3. DEUTERIUM EXCHANGE REACTIONS

Reaction (2)

$$XH^+ + \begin{matrix} D \\ HD \end{matrix} \rightleftharpoons XD^+ + \begin{matrix} H \\ H_2 \end{matrix} \qquad (2)$$
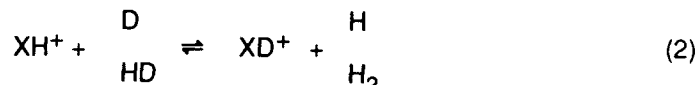
is written to be exoergic according to the empirical rule that, for small species, the exoergic route places the heavier isotope in the larger product species. (Established from the study of many isotope exchange reactions,[9] this rule can fail for larger species[10]). This is a statement that the fractionation of deuterium in interstellar molecules via Reaction (2) is thermodynamically allowed. Since exoergic ion-molecule reactions proceed generally with high reaction efficiency, reaction (2) should incorporate deuterium efficiently into interstellar molecules.
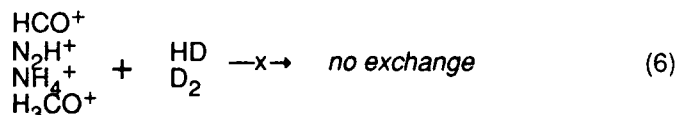
The data tell a different story. Atomic deuterium does exchange efficiently with the few ions that have been studied[11,12]

$$XH^+ + D \rightarrow XD^+ + H \qquad (4)$$

whereas molecular deuterium[13] sometimes does exchange

$$\begin{matrix} H_3^+ \\ CH_3^+ \end{matrix} + \begin{matrix} HD \\ D_2 \end{matrix} \rightarrow \quad exchange \qquad (5)$$

but sometimes does not

$$\begin{matrix} HCO^+ \\ N_2H^+ \\ NH_4^+ \\ H_3CO^+ \end{matrix} + \begin{matrix} HD \\ D_2 \end{matrix} \xrightarrow{\quad x \quad} no\ exchange \qquad (6)$$
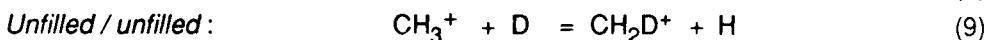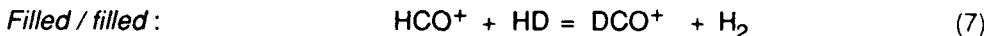
These exoergic reactions (6) fail because of energy barriers in the potential energy hypersurface. In order to be able to distinguish those reactions which can occur from those which cannot, it is necessary to infer from the chemistry the qualitative features of the reaction hypersurface.

## 4. CHARACTERIZING THE REACTION HYPERSURFACE

### 4.1. Reactants with Filled and Unfilled Valence Shells

It is useful to classify the reactants as either having filled or unfilled valence electronic shells. Reactants with filled valence electron shells, possess the electronic configuration characteristic of an inert gas ($s^2$, $s^2p^6$ or $s^2p^6d^{10}$) : examples are $H_2$, $H_3^+$, $N_2$, $N_2H^+$, CO, and $HCO^+$. Examples of species with unfilled valence shells are H, $CH_3^+$ etc. According to this classification, there are three possible combinations of reactants, as shown below with illustrative examples:

*Filled / filled* : $\qquad HCO^+ + HD = DCO^+ + H_2 \qquad (7)$

*Filled / unfilled* : $\qquad HCO^+ + D = DCO^+ + H \qquad (8)$

*Unfilled / unfilled* : $\qquad CH_3^+ + D = CH_2D^+ + H \qquad (9)$

Exoergic isotope exchange reactions that do not occur [ Reaction (6) ] are distinguished by both reactants having filled shells [Reaction (7)]. (This is a necessary but not sufficient condition since reactants with filled shells can still undergo facile exchange, e.g. $H_3^+$ + HD [Reaction (5)].[13])

## 4.2. Basins in the Reaction Hypersurface

Reactants with unfilled valence shells are *electrophilic*, reacting to fill the shells by sharing *electrons*, through forming chemical bonds. Thus for the filled / unfilled example (8), the intermediate is the $H_2CO^+$ -type ion with a binding energy of 1.0 eV. For the unfilled/unfilled case (9), the intermediate is the $CH_4^+$ -type ion with a binding energy of 1.75 eV.[14] The strongly bound intermediate is represented on the hypersurface as a *single, deep basin*, as shown in Figure 1.



$$D + HCO^+ \rightleftharpoons \begin{matrix} H \\ D \end{matrix} C = O^+ - \longrightarrow H + DCO^+$$
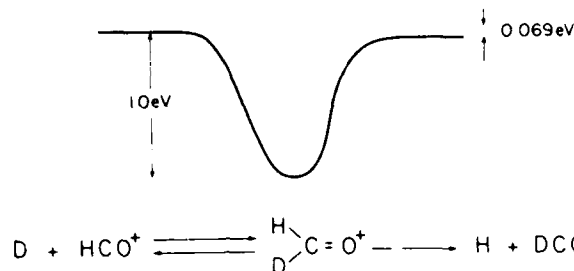
Figure 1.    Representative slice through the reaction hypersurface for deuterium exchange for a reactant with an unfilled valence shell, showing the binding energy of the intermediate and the reaction exoergicity.[4]

Where both reactants $XH^+$ + Y have filled valence shells, there is no chance of strong chemical bonding and no strongly bound intermediates. Intermediates such as $XH^+ \cdot Y$ are bound by purely electrostatic forces — ion-induced dipole and ion-dipole — with binding energies of only a few tenths of an eV.[15] Unlike Figure 1, the hypersurface is not dominated by a single, deep basin. Instead the appropriate hypersurface is that for proton transfer from X to Y, because the minimum energy pathway for isotope exchange involves *internal proton transfer* $XH^+ \cdot Y \leftrightarrow X \cdot YH^+$ within the reaction intermediate. The distinctive features of this hypersurface (Figure 2) are *two shallow basins*, corresponding to the two intermediates $XH^+ \cdot Y$ and $X \cdot YH^+$.



$$XH^+ + Y \rightleftharpoons XH^+ \cdot Y \xrightarrow{H^+} X \cdot YH^+ \longrightarrow X + YH^+$$
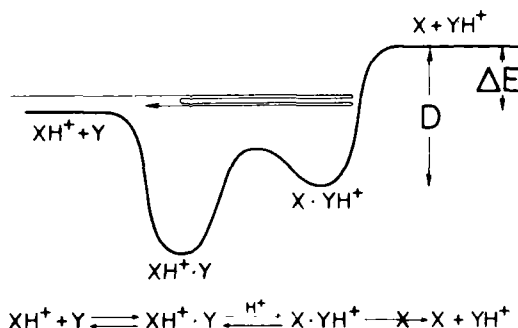
Figure 2.    Representative slice through the reaction hypersurface for deuterium exchange between reactants with filled valence shells. D is the binding energy of the intermediate $X \cdot YH^+$. $\Delta E$, the endoergicity of the proton transfer reaction $XH^+$ + Y → X + $YH^+$, is the difference in proton affinity between Y and X. Exchange is possible if the reactants can reach the second well, i.e. if $\Delta E$ < D. [Such diagrams have been used extensively by ion chemists to describe deuterium exchange reactions.[16]]

## 5. DEUTERIUM EXCHANGE

### 5.1 General Conditions

No barriers inhibit deuterium exchange for exoergic reactions where at least one reactant has an unfilled valence shell. The single deep well in the hypersurface — a consequence of the chemical bonding between the reactants — attracts the reactants to form an intermediate which subsequently dissociates either to give products or to give back reactants (Figure 1). This partitioning gives a negative temperature dependence to the exoergic reaction, such as (1) — the rate constant increasing with decreasing temperature until every collision results in reaction in the limit of absolute zero.



$$HCO^+ + D_2 \rightleftharpoons HCO^+ \cdot D_2 \xrightarrow{\;\;\times\;\;} CO \cdot HD_2^+ \xrightarrow{\;\;\times\;\;} CO + HD_2^+$$
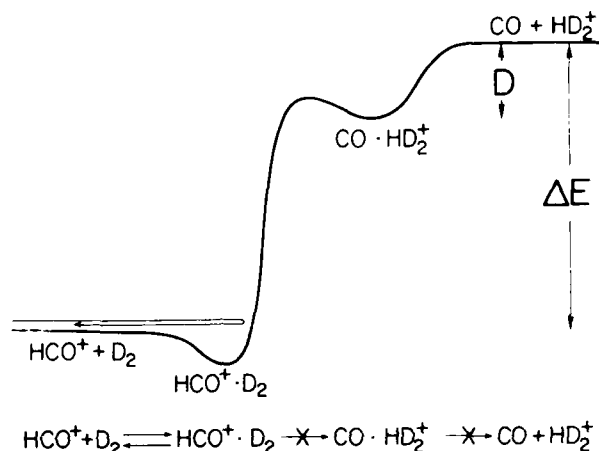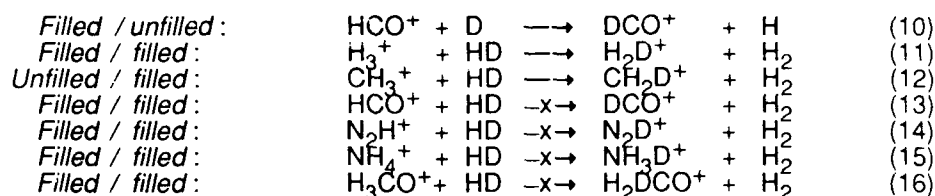
Figure 3.      Representative slice through the reaction hypersurface for deuterium exchange between reactants with filled valence shells, for a system where exchange does not occur. For the system shown, $HCO^+ + HD$, $\Delta E \sim 1.8$ eV and $D \sim 0.5$ eV.[14,15] Because $\Delta E > D$, the second well is inaccessible, so that proton shuttling within the intermediate is not possible.

In contrast, barriers can inhibit deuterium exchange wherever both reactants show filled valence shells. For the reactants $XH^+ + Y$ to undergo exchange by the internal proton transfer or shuttling mechanism (Figure 2), the corresponding proton transfer reaction $XH^+ + Y \rightarrow X + YH^+$ reaction must be endoergic, i.e. $\Delta E > 0$. For deuterium exchange to be possible by this mechanism, the second basin, $X \cdot YH^+$, must be accessible to the reactants, i.e. $D > \Delta E$. Figure 3 shows a representative example where this condition is not met.

Reaction rate constants show the same negative temperature dependence for the double-basin mechanism (Figure 2)[17] as they do for the single-basin mechanism (Figure 1).[11]

### 5.2. Applications to Interstellar Chemistry

Using the guidelines developed above, we can now re-examine the deuterium exchange reactions that succeed (4,5) and fail (6).

| | | | | | | |
|---|---|---|---|---|---|---|
| Filled / unfilled : | $HCO^+$ + D | $\longrightarrow$ | $DCO^+$ | + | H | (10) |
| Filled / filled : | $H_3^+$ + HD | $\longrightarrow$ | $H_2D^+$ | + | $H_2$ | (11) |
| Unfilled / filled : | $CH_3^+$ + HD | $\longrightarrow$ | $CH_2D^+$ | + | $H_2$ | (12) |
| Filled / filled : | $HCO^+$ + HD | $-x\rightarrow$ | $DCO^+$ | + | $H_2$ | (13) |
| Filled / filled : | $N_2H^+$ + HD | $-x\rightarrow$ | $N_2D^+$ | + | $H_2$ | (14) |
| Filled / filled : | $NH_4^+$ + HD | $-x\rightarrow$ | $NH_3D^+$ | + | $H_2$ | (15) |
| Filled / filled : | $H_3CO^+$+ HD | $-x\rightarrow$ | $H_2DCO^+$ | + | $H_2$ | (16) |

In deuterium exchange reactions of the type $XH^+ + HD \rightarrow XD^+ + H_2$, where X is a stable molecule such as $N_2$, $NH_3$ etc., both reactants show filled shells. Consequently, energy barriers stop Reactions (13) - (16) because the proton affinity of $H_2$ is less than that of the other species X. The lowest value found for $\Delta E$ is 0.7 eV, the value for Reaction (14).[14] Even this exceeds the binding energy D of the intermediate $H_2D^+.X$, which is not more than ~ 0.5 eV.[15] Thus the condition $\Delta E > D$ consistently prevails so that access to the second basin — and deuterium exchange — are not possible (Figure 3). Exceptions arise where the reaction is symmetric, requiring that $\Delta E \sim 0$, that necessarily $\Delta E < D$ and therefore the absence of any barrier to deuterium exchange. Reaction (11) is one example of a symmetric reaction[13] and the reaction $D^+ + H_2 \rightarrow H^+ + HD$ is another.[18]

In contrast, for Reactions (10) and (12) there are no barriers to deuterium exchange. Each shows one reactant with an unfilled valence shell ; each forms an intermediate which is chemically bound and which features as a single deep well in the hypersurface. (For (10) see Figure 1 : for (12) the binding energy of the $CH_5^+$ -type intermediate is ~ 2 eV.[14])

Laboratory measurements support these conclusions consistently. Thus $HCO^+$ and $N_2H^+$ exchange readily with D but not with $D_2$ ;[11] both $CH_3^+$ and $H_3^+$ exchange with HD ;[13] and the predicted negative temperature dependence is found. In certain cases the laboratory measurements have only explored deuterium exchange with $D_2$ but not with HD. Our description shows that what is found for $D_2$ must apply equally to HD.

In conclusion, it may be appropriate to emphasize the importance of Reaction (1) as a pathway for deuterating interstellar molecules. It synthesizes in a single step deuterated species of the same complexity as the starting material ; and, as the deuterating agent, it uses deuterium atoms, the primary source of deuterium. Thus it would appear to provide possible routes for the synthesis of CCD [8] via $C_2H_2^+ + D \rightarrow C_2HD^+ + H$ and for the synthesis [6] of $C_3HD$ via $C_3H^+ + D \rightarrow C_3D^+ + H$.[19]

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